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MODELS FOR FITTING VOLUME-TEMPERATURE DATA

A key physical parameter for modelling the response of crystalline material as a function of the applied temperature is the volume (V) thermal expansion coefficient α_V , defined as $(1/V) \cdot (\partial V / \partial T)_P$. The latter can be derived from the curve that describes V as f(T). Because such a derivation is model dependent, it is appropriate to consider what model is most suitable in fitting experimental V-T data.

A fit to high temperature volume data should include a number of important features:

(a) It should give a good fit to the data as judged by parameters such as χ^2 or R^2 . Ideally, the deviations of the fit should, on average, be less than the average of the experimental error. (b) It should accurately predict experimental data below and above the temperature measurement range, which commonly lies between room temperature and the highest temperature achieved by commercial heating systems, 900 °C or more. (c) It should be based on a physical model using variables that can be measured by other techniques, for example the bulk modulus as well as the Einstein and Debye temperatures, and produce output having physically sensible results. (d) It should neither over- or under-parameterize the data. For example, if V-T data allow a linear fit only, higher-order models can result in non-physical or meaningless extrapolation to higher or lower temperatures. Generally, the statistically best model requiring the fewest parameters should be utilized.

In principle, a physical model is most desirable. Because thermal expansion is related to the vibrational energy of a crystal, the latter potentially provides information on the energetics of the substance. According to Wallace (1998) and Knight and Price (2008), the energy of lattice vibrations (U) changes with volume as

$$(1) V = V_0 + U\gamma/K$$

where γ is the Grüneisen parameter and K_0 the bulk modulus at 0 K. The energy of lattice vibrations can be obtained through an Einstein model for the latter

$$(2) U = 3Nk_B\theta_E/(e^{\theta_E/T}-1)$$

or a Debye model

$$(3) U = 9Nk_BT(T/\theta_D)^3$$

where N is the number of atoms in the unit cell, k_B the Boltzmann constant and θ_E and θ_D the Einstein and Debye temperatures, respectively, which are related to the period ω of the Einstein and Debye oscillators.

The Einstein and Debye models differ in the way they describe the vibrational spectrum (Wallace 1998). In the Einstein model the quantity $k = 3Nk_B\theta_E\gamma/K_0$ may be refined as a single parameter, so that the equation for linear change of lattice energy with temperature becomes

$$(4) V = V_0 + k/(e^{\theta_E/T}-1)$$

The latter has just three refinable parameters V_0 , k and θ_E , which have been utilized, for example, by Redhammer et al. (2010). Equation (4) assumes a linear relationship between volume and lattice energy, which is an approximation to the original power series expansion in the Mie-Grüneisen equation of state (Grüneisen 1912; Anderson et al. 1992).

Different models have been proposed to account for a non-linear relationship between volume and lattice energy, including those proposed by Wallace (1998), Suzuki et al. (1979) and Kumar (2003), as discussed at length by Kroll et al. (2012). These models have been used for minerals, for example, in modelling data for synthetic richterite (Tribaudino et al. 2008a), plagioclase (Tribaudino et al. 2011) and olivine (Kroll et al. 2012). Although such models are typically referred to a temperature of absolute zero, for petrologic modelling involving temperatures far above 0 K, Holland and Powell (2011) proposed a scaled Einstein-like formulation for lattice energy in which room-temperature volume and thermal expansion can be refined for any condition. Here, relations of volume with temperature are explicitly written as

$$(5) V = V_{298} \{ 1 - \alpha_{298} K' \theta_E (e^{\theta_E/298} - 1)^2 / [(\theta_E/298)^2 e^{\theta_E/298}] [1/(e^{\theta_E/T} - 1) - 1/(e^{\theta_E/298} - 1)] \}^{-1/K'}$$

(Tribaudino et al. 2011). Required parameters V_{298} , α_{298} , K' and θ_E in the latter are room-T volume, room-T thermal expansion coefficient, room-T first derivative of the bulk modulus, and Einstein temperature, respectively. A different, but equivalent, formulation has been used by Holland and Powell (2011) and implemented in the EosFit7c code of Angel et al. (2014), who showed substantial equivalence with the formulation according to the Kumar formalism proposed by Kroll et al. (2012). Just as for the Eosfit7 code, we shall refer to this as the "Kroll" equation for the remainder of this paper.

A sensible refinement of one of the physical models requires data that accurately describe deviations from linear V-T behavior, which are most apparent at low temperature (Fig. 1). Indeed, either the lack of closely-spaced precise data above room T or the absence of such data below room T can result in significant analysis errors. This is due to the fact that parameters refined in physical models are highly correlated; without truly robust data, values for θ_E and K' cannot be reliably refined. In practice, however, one can estimate the Einstein temperature in eqn. (5) through tabulated room-temperature entropy data (e.g., Holland and Powell, 2011) as $\theta_E = 10636/(S_{298}/n + 6.4)$, where n is the number of atoms in the chemical formula of the relevant substance. Moreover, values of K' are generally available from experimental investigations at high pressure (P). V_{298} and α_{298} , of course, can be obtained from experimental V-T data. It should be noted that for the description of V-T variation within an experimental range, the choices of θ_E and K' values are not critical (Angel et al. 2014).

A different approach to data characterization utilizes empirical models. For the latter, equations simply describe V-T behavior without any assumption about physical parameters. Although these are more robust in giving a result unaffected by the choice of the starting parameters, they may be inappropriate to data or lack physical meaning. Various such models have been proposed by Berman (1988), Pawley et al. (1996), Fei (1995), and Salje et al. (1991), as

discussed by Angel et al. (2014). The simplest of these assumes that thermal expansion is constant with temperature:

$$(6) \ln(V/V_0) = \alpha(T-T_0)$$

In practice, thermal expansion and T_0 obtained from eqn (6) are equivalent to one obtained by a linear fit between V/V_0 and temperature (Angel et al. 2014). Thus, we shall refer to eqn. (6) as "linear." Indeed, straight-line V-T approximations are useful when only a limited number of data points are available, such as those of early pioneering papers on pyroxene thermal expansion by Kozu and Ueda (1933), Deganello (1973), and Cameron et al. (1973). Because changes in thermal expansion are relatively small at higher temperatures, the approximation of a fixed thermal expansion coefficient as $f(T)$ is useful in cases where a more detailed analysis is not possible.

A more complex, yet empirical, formulation for V-T data has been provided by Fei (1995):

$$(7) V=V_0 \exp(a_0(T-T_{\text{ref}})+1/2a_1(T^2-T_{\text{ref}}^2)-a_2(1/T-1/T_{\text{ref}}))$$

(Angel et al. 2014 from Fei 1995). The first derivative of this equation gives the thermal expansion coefficient at any temperature as

$$(8) \alpha_T = a_0 + a_1 T + a_2/T^2$$

Successful determination of the a_2 term in this model requires high-quality data. Inability to determine the a_2 term results in linear α vs. T results. Such an approximation is found in the second-order polynomial model of Berman (1988):

$$(9) V/V_0 = 1 + a_1(T-T_0) + a_2(T-T_0)^2/2$$

where the thermal expansion coefficient varies with T as

$$(10) \alpha = a_1 + a_2(T-T_0)$$

In order to model the non-linear behavior of thermal expansion, yet reduce the number of parameters to be refined, the first version of the widely used Holland and Powell (1998) thermodynamic data base alternatively proposed a single-parameter model, first introduced by Pawley et al. (1996):

$$(11) V/V_0 = 1 + a^\circ(T-T_0) + 20a^\circ(\sqrt{T}-\sqrt{T_0})$$

Here, thermal expansion at a given T is calculated as $\alpha = a^\circ(1-10/\sqrt{T})$. This model, later discarded in the Holland and Powell (2011) database, was replaced by one based on physical quantities. A modified version of the model from Angel et al. (2014) was used by Pandolfo et al. (2015) to fit data for jadeite-diopside pyroxenes.

It should be noted that, even when empirical models successfully model the saturation of thermal expansion at relatively high T, they fail to accurately describe the variation of thermal expansion at low temperature, i.e., $T < 100\text{K}$ (Angel et al. 2014).